

Transparent conducting thin films of GaInO_3

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GaInO_3 is recently identified transparent conducting material which is structurally and chemically distinct from indium tin oxide [R. J. Cava, J. M. Phillips, J. Kwo, G. A. Thomas, R. B. van Dover, S. A. Carter, J. J. Krajewski, W. F. Peck, Jr., J. H. Marshall, and D. H. Rapkine, *Appl. Phys. Lett.* **64**, 2071 (1994)]. We have used both dc reactive sputtering in the on- and off-axis geometries and pulsed laser deposition to grow films of this material. Layers of pure GaInO_3 as well as those partially substituted with Ge for Ga or Sn for In have been studied. Both growth techniques are capable of producing films with conductivity $\sim 400 (\Omega \text{ cm})^{-1}$ and transmission as high as 90% throughout the visible spectrum for $\sim 1\text{-}\mu\text{m}$ -thick films. The growth techniques differ in the morphology of the films produced as well as in the degree of dopant incorporation that can be achieved. A post-growth anneal in H_2 can help produce an optimized oxygen content and a reduction of resistivity. Hall measurements indicate a carrier concentration up to $4 \times 10^{20} \text{ cm}^{-3}$ for all films and a Hall mobility up to $10 \text{ cm}^2/(\text{V s})$. Doping appears to be due both to oxygen vacancies and aliovalent ion substitution.

A number of transparent conducting oxides (TCO) such as indium tin oxide ($\text{In}_2\text{O}_3\text{:Sn-ITO}$), ZnO:Al , and $\text{SnO}_2\text{:F}$ have been investigated extensively.¹⁻⁵ Indium tin oxide (ITO) has become the TCO of choice for a wide variety of applications from solar cells to flat panel displays for at least 20 years.¹⁻³ Typical ITO films have a sheet resistance of $10 \Omega/\square$ [i.e., a conductivity of about $2.5\text{--}5 \times 10^3 (\Omega \text{ cm})^{-1}$]. Future designs will require a sheet resistance approaching $1 \Omega/\square$. This cannot be accomplished simply by increasing the thickness of the ITO, since the thicker film would have unacceptable transmission characteristics. Even given a sheet resistance in the neighborhood of $10 \Omega/\square$, there is a need for a conductor with better transparency across the visible spectrum, especially in the green-blue region. These challenging goals require a major improvement in the materials used as transparent conductors.

GaInO_3 is a recently identified transparent conductive material.⁶ It is structurally distinct from ITO, having a $\beta\text{-Ga}_2\text{O}_3$ structure with the Ga site tetrahedrally coordinated and the In site octahedrally coordinated. Aliovalent elements such as Ge or Sn and/or oxygen vacancies dope these materials to achieve conductivities of over $300 (\Omega \text{ cm})^{-1}$ as discussed below. In bulk polycrystalline form, the resistivity is comparable to conventional wide-band-gap transparent conductors such as ITO while exhibiting superior light transmission, particularly in the blue wavelength region of the visible spectrum, and enhanced index matching with typical glass substrates used in the fabrication of flat panel displays.

While the bulk material exhibits highly promising qualities, the primary use of transparent conductive materials is as coatings on transparent substrates such as glass, fused silica, plastic, and semiconductors. In this letter we report the growth and properties of GaInO_3 films deposited on glass and quartz substrates by both sputtering and pulsed laser deposition (PLD).

The targets employed for thin film growth were prepared by standard ceramic processing methods. Starting materials

were powdered Ga_2O_3 , In_2O_3 , GeO_2 , and SnO_2 mixed in the appropriate molar proportions to yield $\text{Ga}_{1-x}\text{Ge}_x\text{InO}_3$ or $\text{GaIn}_{1-x}\text{Sn}_x\text{O}_3$, for $0 \leq x \leq 0.20$. Powders were initially fired for two 15 h periods in air at 1300°C with intermediate grindings. Targets of the appropriate size were pressed in steel dies and then fired for an additional 15 h period at 1300°C in air. Two different final firing steps were found to be satisfactory in chemically reducing the samples from their air-fired state to yield the desired high conductivity material before use as targets. In one, the targets were heated at 1200°C in Zr gettered flowing N_2 at 1200°C for 15 h. In the other, a 1 h treatment at $550\text{--}600^\circ\text{C}$ in a more reducing $15\%\text{H}_2\text{--}85\%\text{N}_2$ mixture was found to yield equivalent or slightly superior results.

GaInO_3 films nominally doped with between 5% and 15% Sn on the In site were deposited by dc reactive sputtering in both on-axis and off-axis sputtering configurations. The placement of substrates outside the plasma plume in the so-called 90° off-axis geometry avoids the bombardment of negative oxygen ions and gives tighter control of the stoichiometry, resulting in better film conductivity. However, it also tends to yield a higher degree of thickness nonuniformity than the on-axis sputtering configuration. The total pressure ($\text{Ar} + \text{O}_2$) during growth is kept in the range of $5\text{--}10$ mTorr in both cases. The oxygen partial pressure during growth plays the most critical role in governing the phase stability and film quality. The optimal O_2 pressure is about $0.5\text{--}1.0$ mTorr. Higher O_2 partial pressure produces transparent, yet more resistive films. In contrast, sputtering with no added O_2 yields black, insulating films. Crystalline films of the correct phase can be formed even at room temperature; however, as-grown films with the lowest resistivity are usually obtained at substrate temperatures in the range of $350\text{--}400^\circ\text{C}$. A complete account of the synthesis of GaInO_3 films by the sputtering method will be given elsewhere.^{7,8}

PLD deposited films were grown using a target of either pure or doped (up to 10% Sn for In or Ge for Ga) GaInO_3 . A

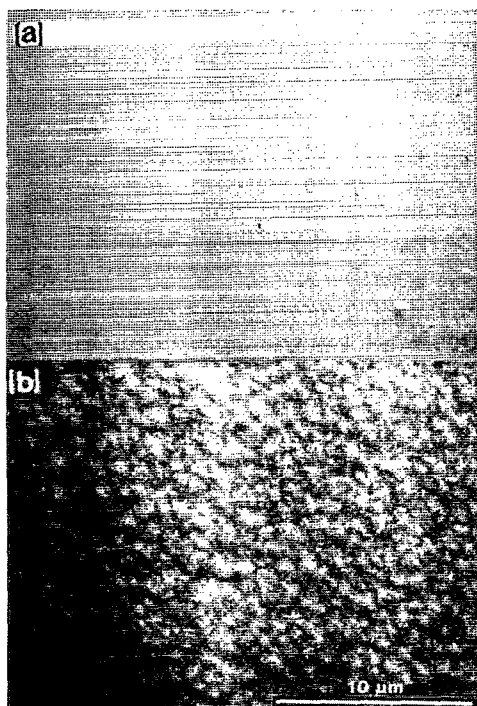


FIG. 1. SEM micrographs comparing the morphology of GaInO₃ films grown by sputtering and PLD. (a) Film doped with 5% Sn grown by sputtering; (b) film doped with 5% Sn grown by PLD.

KrF excimer laser operating at 248 nm with a repetition rate of 10 Hz was used. 2 J/cm² energy density was incident on the target. The deposition chamber had a base pressure of 1×10^{-7} Torr. During growth, the O₂ pressure was maintained between 0 and 100 mTorr. The substrate temperature was varied between room temperature and 400 °C. Both the oxygen pressure and substrate temperature are important parameters in dictating film transparency and conductivity as will be discussed at length elsewhere.^{9,10} Films with highest conductivity and only slightly suboptimum transparency were grown at a substrate temperature of 250 °C in an oxygen pressure of 1 mTorr. X-ray diffraction shows only GaInO₃ peaks in these films.

Films were characterized for their morphology, optical, and conducting properties. As seen in Fig. 1, scanning electron microscopy (SEM) shows films deposited by off-axis sputtering to be very smooth, although the precipitate density is notably high for films doped with 15% Sn. PLD-deposited films, on the other hand, show a somewhat granular microstructure but no evidence for precipitates at any dopant concentration up to 10%. These results suggest that the cation doping by Sn in GaInO₃ may have a solubility limit lower than in In₂O₃, dependent on the synthesis method.

The transmittance spectra of GaInO₃ films have been measured for films of various doping concentrations and a variety of deposition conditions. In general, the far-infrared absorption and the dc conductivity vary together with the O₂ pressure during deposition.¹¹ The visible and near infrared transmittance shows Fabry-Perot oscillations that allow a determination of the index of refraction as 1.65 ± 0.1 . This is a considerably closer match to the index of refraction of

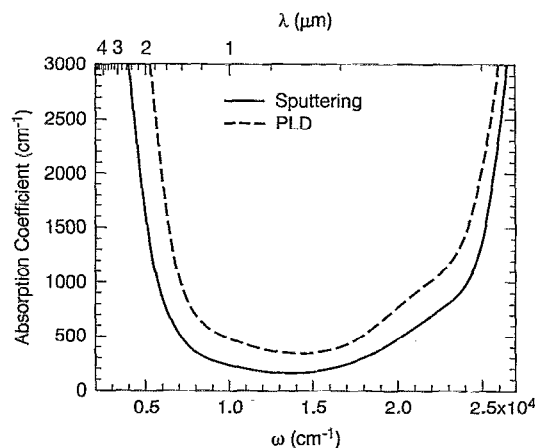


FIG. 2. Absorption coefficients of an off-axis sputtered film ($\sigma \sim 170 \Omega \text{ cm}^{-1}$) and a PLD film ($\sigma \sim 280 \Omega \text{ cm}^{-1}$).

glass (~ 1.5) than that of ITO, which is about 2.⁶ As seen in Fig. 2, the absorption coefficient is smallest at $< 500 \text{ cm}^{-1}$ near a wavelength of 600 nm for a film with a dc resistance of $42 \Omega/\square$ [$\sigma = 280 (\Omega \text{ cm})^{-1}$]. The high frequency absorption shows an energy gap near 3.3 eV (380 nm). The absorption coefficient of GaInO₃ is significantly lower over the entire visible range than that of commercially available ITO ($\geq 1000 \text{ cm}^{-1}$), ZnO:Al ($3000\text{--}20\,000 \text{ cm}^{-1}$),⁴ or SnO₂:F ($> 10\,000 \text{ cm}^{-1}$).⁵

The temperature-dependent resistivity as well as the room-temperature Hall constant and magnetoresistance were measured in the van der Pauw configuration using chopped dc at $\sim 1 \text{ A/cm}^2$. For example, GaIn_{0.94}Sn_{0.06}O₃ deposited at 250 °C by PLD in a 1 mTorr O₂ ambient yields a room-temperature conductivity of $345 (\Omega \text{ cm})^{-1}$, about 3–10 times lower than that of the best transparent conducting films currently available.^{1–5} For this film, the temperature coefficient of resistivity (TCR) is $1.5 \mu\Omega \text{ cm/K}$, indicating the metallic nature of the material. Below about 120 K the TCR changes sign, which may reflect either localization or inhomogeneity (e.g., increased resistivity at grain boundaries). The sign of the Hall constant is negative in all samples, indicating electron conduction, as expected for oxygen-vacancy doping or Sn (or Ge) doping. Thermoelectric measurements are consistent with electron-like carriers. The magnitude of the Hall constant does not vary systematically with the nominal dopant metal stoichiometry, suggesting both the presence of oxygen vacancies whose concentration depends on synthetic conditions and trapping of free carriers (compensation). Typical carrier densities inferred from the Hall constant are in the range $1 \times 10^{19}\text{--}4 \times 10^{20} \text{ cm}^{-3}$, comparable to or slightly lower than the values quoted for other transparent conductors.^{1–5} The magnetoresistance is typically less than $0.2 \mu\Omega \text{ cm/T}^2$.

In an attempt to increase the conductivity, the samples were annealed in various environments. The measurements were performed *in situ* using a standard four-probe technique, silver paint contacts, and platinum wire leads. Annealing in air, N₂, Ar, O₂, or 1–10 mbar partial-pressure O₂ in Ar always leads to a decrease in the conductivity. This decrease

TABLE I. Conductivities of representative sputtered and PLD films of $\text{GaIn}_{1-x}\text{Sn}_x\text{O}_{3+\delta}$ prepared from regular and reduced targets, both as-grown and after annealing in vacuum or H_2/N_2 . In general, annealing in a reducing atmosphere increases conductivity. There is a weak tendency for conductivity to increase as the Sn content increases.

x	$\sigma(\Omega \text{ cm})^{-1}$	Growth technique	Vacuum anneal	H_2/N_2 anneal	Reduced target
0	175(15)	PLD		X	
	150(15)	PLD			
0.05	230(20)	PLD	X		
	230(20)	S		X	
	215(20)	PLD		X	
	170(20)	PLD	X		
	170(20)	S			
	80(20)	PLD			
	70(10)	S			
0.06	365(15)	PLD		X	X
	345(15)	PLD			X
0.15	315(20)	S		X	
	260(20)	S			
	150(15)	PLD			X
0.20	300(50)	S			X

begins when the temperature exceeds 200 °C and becomes greater with increasing temperature. This appears to be due to the diffusion into the sample of O_2 , which is inadvertently present in the experimental apparatus, filling oxygen vacancies present in as-grown films. Samples annealed in 0.1% H_2/Ar show very little change in the conductivity. Annealing in a suitable oxygen reducing environment, such as forming gas (15% $\text{H}_2/85\% \text{N}_2$) leads to an increase in the conductivity. The conductivity is maximized by annealing for 4–5 h at 280–300 °C and ~200 ml/min of flowing forming gas. Higher temperatures and flow rates lead to no improvement. In most cases, temperatures above 320 °C and annealing times greater than 5 h result in decreased conductivities. The annealing improves by over two orders of magnitude for the low conductivity samples [$<0.1 (\Omega \text{ cm})^{-1}$], but has less than a 10% effect on the highest conductivity samples [$300 (\Omega \text{ cm})^{-1}$]. Table I shows the conductivities of representative sputtered and PLD films annealed in a variety of ambients. The highest conductivities occur in reduced $\text{GaIn}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ samples, the magnitude being only weakly dependent on the

Sn doping. The removal of oxygen through reduction has a larger effect on the conductivity than changing the concentration of a cation dopant. The higher conductivities could result from an increase in the number of electrons at the cation sites, as reflected by the larger carrier densities ($>2 \times 10^{20} \text{ cm}^{-3}$) derived from Hall measurements on the reduced target samples. However, the Hall mobilities vary greatly between samples, tending to be slightly higher for the post-annealed samples. This makes it difficult to generalize the effect of reduction on the density of carriers. Nonetheless, the annealed and reduced target samples tend to have similar conductivities when the Sn doping exceeds 5%, and further annealing in forming gas does not improve the conductivity past the highest obtained value of $300 (\Omega \text{ cm})^{-1}$.

We have shown that GaInO_3 is a promising TCO that can be grown by dc reactive sputtering and by PLD. Doping results from oxygen vacancies and/or substitution of aliovalent elements such as Ge or Sn. The optical transmission characteristics are significantly better than those of state of the art TCOs. This makes it possible to consider the use of thicker films to compensate for the somewhat higher resistivity of GaInO_3 compared with other TCOs. We are hopeful that improved understanding of the details of the doping of GaInO_3 will enable us to further improve film resistivity while preserving the already excellent transparency.

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